
(12) UK Patent Application (19) GB (11) 2044 768 A

(21) Application No 8007667

(22) Date of filing
6 Mar 1980

(30) Priority data

(31) 79/08767

(32) 13 Mar 1979

(33) United Kingdom (GB)

(43) Application published
22 Oct 1980

(51) INT CL³ C07C 21/22

(52) Domestic classification
C2C 202 20Y 311 31X
31Y 43X 565 569 AB
HJ

(56) Documents cited
None

(58) Field of search
C2C

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(54) Preparation of 1,1,1, 4,4,4-hexafluorobutyne

(57) A process for the preparation of

F-2-butyne which can be polymer-

ized to yield fluorinated polymers of

high thermal stability which comprises contacting F-cyclobutene with a source of fluoride ions, preferably caesium fluoride, under anhydrous conditions at a temperature of from 450°C to 650°C, for example by passing the F-cyclobutene through a heated tube packed with the source of fluoride ions.

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SPECIFICATION

Preparation of F-2-butyne

5 This invention relates to the preparation of F-2-butyne ($F_3C.C\equiv C.CF_3$) and particularly to a process for the preparation of F-2-butyne from F-cyclobutene (perfluorobutene).

10 According to the present invention there is provided a process for the preparation of F-2-butyne which comprises contacting F-cyclobutene with a source of fluoride ions under anhydrous conditions at a temperature greater than 450°C.

15 The F-cyclobutene can be contacted with the source of fluoride ions by passing it through a tube, for example a metal, e.g. nickel tube packed with the source of fluoride ions and heated at the desired temperature.

20 The rate of flow of the F-cyclobutene through the packed tube can be controlled so as to provide the optimum contact time of the F-cyclobutene with the source of fluoride ion for maximum conversion to F-2-butyne. Usually

25 the F-cyclobutene will be diluted before passage through the tube by an inert diluent or carrier gas, for example nitrogen gas, a typical dilution being about 1:30. By way of example and as a guide only we have found that a rate 30 of flow of gas through the tube such as to provide a contact time of the order of 20 seconds is suitable for most purposes.

35 The temperature of the source of fluoride ions, i.e. the temperature at which the F-cyclobutene is contacted with fluoride ions, is usually above 450°C and is preferably greater than 500°C. Especially preferred are temperatures in excess of 550°C, for example from 550°C to 600°C. Increasing the temperature 40 above 650°C is undesirable in that there is a tendency for the F-2-butyne product to form by-products. Accordingly we prefer to carry out the process at below 650°C. Below about 650°C, increasing the temperature results in 45 general in an increase in the percentage conversion of the F-cyclobutene to F-2-butyne.

50 Any source of fluoride ions may be employed which provides fluoride ions at a temperature in the range of from 450°C to 650°C, for example caesium fluoride and potassium fluoride. We prefer to employ caesium fluoride. Since the process of the invention is carried out under anhydrous conditions the source of fluoride ions should be dried if 55 necessary before the F-cyclobutene is contacted with it. Drying can be effected, for example, by heating the source to the desired temperature (450°C to 700°C) in a stream of nitrogen gas prior to feeding the F-cyclobutene to the source.

60 The F-2-butyne product ($B_p-25^\circ C$) can be polymerized and copolymerized by free-radical polymerization to yield a fluorinated polymer of high thermal stability. For example polymers are obtainable which are resistant to tem-

peratures of 100°C higher than the decomposition temperature of polytetrafluoroethylene. Homopolymers of F-2-butyne do not exhibit a crystalline melting point below their decomposi-

70 tion temperature and cannot be melt-processed, but they can be used as fillers for melt-processable polymers or they can be formed *in situ* as coatings for example on a variety of substrates. Upon prolonged heating F-2-bu-

75 tyne trimerises to yield hexa(trifluoromethyl) benzene. A further use of F-2-butyne is in the production of transition metal complexes.

80 The invention is illustrated but in no way limited by the following examples in which percentages are by weight:—

EXAMPLE 1

F-cyclobutene (5.9g) was passed in a stream of nitrogen gas through a nickel tube 85 packed with dry, powdered caesium fluoride heated at 510°C. The rate of flow of the gas stream was such that the average contact time of the gas with the caesium fluoride was 20 seconds. The gas stream emerging from the 90 tube was transferred under vacuum to a flask fitted with a variable reservoir. The product was degassed in the flask.

The products (4.7g) were identified by gas-liquid chromatography (gas density balance) 95 and infra-red spectroscopy as unreacted F-cyclobutene (60%) and F-2-butyne (40%).

EXAMPLE 2

The procedure described in Example 1 was 100 repeated using 4.0g of F-cyclobutene and a temperature of 590°C. The products were identified as described as F-cyclobutene (10%) and F-2-butyne (90%).

Repeating the procedure at temperatures of 105 530°C, 550°C and 570°C yielded mixtures of F-cyclobutene and F-2-butyne in approximate percentage ratios of 50:50, 40:60 and 20:80.

110 EXAMPLE 3

The procedure described in Example 1 was repeated except that the tube contained dry powdered potassium fluoride instead of caesium fluoride. At 510°C, F-cyclobutene (6.3g) 115 yielded a mixture (4.7g) of F-cyclobutene (90%) and F-2-butyne (10%).

EXAMPLE 4

The procedure described in Example 3 was 120 repeated at a temperature of 560°C. F-cyclobutene (4.5g) yielded a mixture (3g) of F-cyclobutene (20%) and F-2-butyne (80%).

EXAMPLE 5

125 The procedure described in Example 3 was repeated at a temperature of 640°C. At this temperature F-cyclobutene yielded a mixture containing F-2-butyne (90%).

130 CLAIMS

1. A process for the preparation of F-2-butyne which comprises contacting F-cyclobutene with a source of fluoride ions under anhydrous conditions at a temperature greater than 450°C.
2. A process as claimed in Claim 1 in which the temperature is greater than 500°C.
3. A process as claimed in Claim 1 or Claim 2 in which the temperature is below 650°C.
4. A process as claimed in any one of Claims 1, 2 and 3 in which the source of fluoride ions is caesium fluoride.
5. A process as claimed in any one of the preceding claims in which the F-cyclobutene is diluted with an inert diluent prior to contact with the source of fluoride ions.
6. A process as claimed in Claim 5 in which the dilution of the F-cyclobutene is up to 1:30.
7. A process as claimed in any one of the preceding claims in which the F-cyclobutene is passed through a heated tube packed with the source of fluoride ions.
8. A process as claimed in Claim 7 in which the F-cyclobutene is passed through the tube at a rate such as to provide ions of the order to 20 seconds.
9. A process as claimed in any one of the preceding claims which includes the further step of free-radical polymerization of the F-2-butyne to produce a fluorinated polymer of high thermal stability.
10. A process for the preparation of F-2-butyne substantially as described herein with reference to any one of the examples.

Printed for Her Majesty's Stationery Office
by Burgess & Son (Abingdon) Ltd. 1980.
Published at The Patent Office, 26 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.